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Electronic Supplementary Information

Determination of the microstructure, energy levels and magnetic dipole transition mechanism for Tm^{3+} doped Yttrium aluminum borate

Meng Ju,[ab] Xiao-Yu Kuang,[a*] Cheng Lu,[bc*] Hui Li,[d] Jing-Jing Wang,[a] Chuan-Zhao Zhang[a]

Yong-Sheng Zhu[b] and Yau-Yuen Yeung[e*]

[a] Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, China

[b] Department of Physics, Nanyang Normal University, Nanyang 473061, China

[c] Department of Physics and High Pressure Science and Engineering Center, University of Nevada, Las Vegas, Nevada 89154, USA

[d] Laboratoiré Aime Cotton, CNRS, Université Paris-Sud, ENS Cachan, Orsay 91405, France

[e] Department of Science and Environmental Studies, The Hong Kong Institute of Education, 10 Lo Ping Road, Tai Po, NT, Hong Kong, China

*Correspondence author. E-mail: scu_kuang@163.com (Xiao-Yu Kuang), lucheng@calypso.cn (Cheng Lu) and yyyeung@ied.edu.hk (Yau Yuen Yeung)

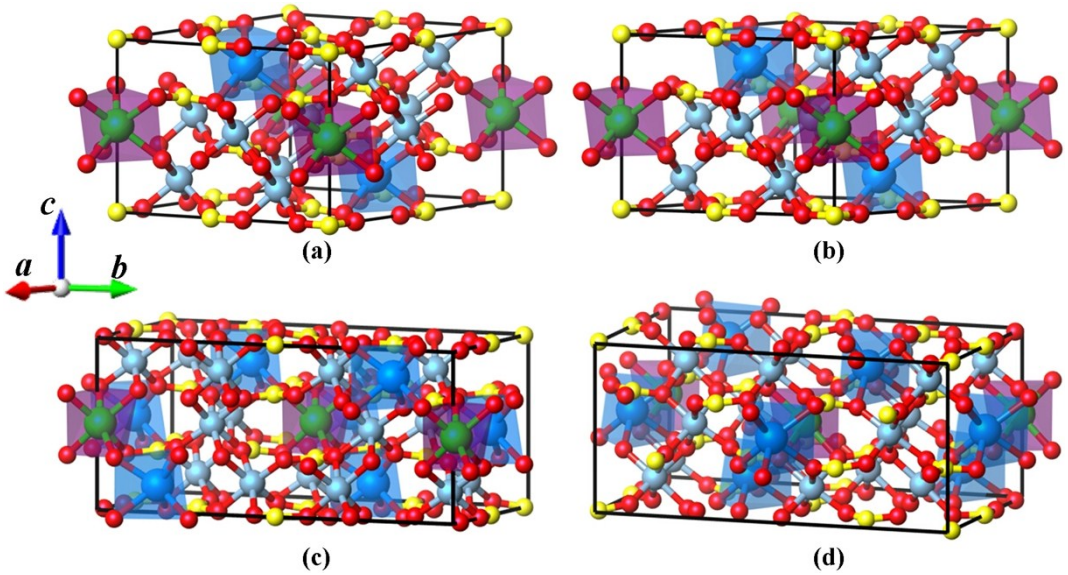

Fig. S1. Coordination structures the optimized low-lying Tm:YAB. The yellow, red, gray, blue and green spheres represent B, O, Al, Y and Tm atoms, respectively.

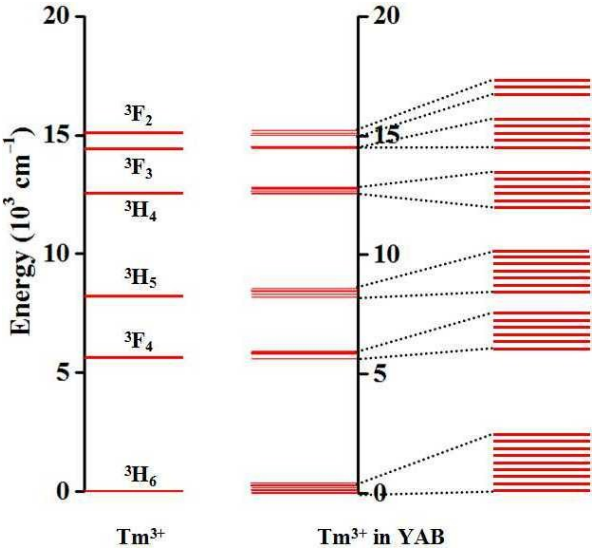

Fig. S2. The calculated energy levels of the free ion Tm^{3+} and Tm^{3+} in YAB crystal.

Table S1. Interatomic distances (Å) in the ground state structure of Tm:YAB. Available experimental results of YAB are also listed for comparision.

Tm-prism	Theor.	Expt. [a]	Al octahedron	Theor.	Expt. [a]	B_1 triangle	Theor.	Expt. [a]
Tm-O(6)	2.338	—	$Al\text{-}O_1(2)$	1.876	1.837	$B_1\text{-}O_1(3)$	1.391	1.383
$O_1\text{-}O_2(6)$	3.297	—	$Al\text{-}O_2(2)$	1.935	1.922	$O_1\text{-}O_2(3)$	2.409	2.396
$O_1\text{-}O'_1(3)$	2.771	—	$Al\text{-}O_3(2)$	1.949	1.938			
Aver.	2.808	—	Aver.	1.920	1.899	Aver.	1.900	—
Y-prism						B_2 triangle		
Y-O(6)	2.337	2.321	$O_1\text{-}O_2(2)$	2.440	2.421	$B_2\text{-}O_1(1)$	1.369	1.367
$O_1\text{-}O_2(6)$	3.290	3.256	$O_1\text{-}O_3(2)$	2.640	2.706	$B_2\text{-}O_2(1)$	1.374	1.373
$O_1\text{-}O'_1(3)$	2.777	2.776	$O_2\text{-}O_3(2)$	2.811	2.706	$B_2\text{-}O_3(1)$	1.395	1.371
			$O_1\text{-}O'_1(2)$	2.838	2.767	$O_1\text{-}O_2(1)$	2.434	2.432
			$O_2\text{-}O'_3(2)$	2.733	2.608	$O_2\text{-}O_3(1)$	2.362	2.345
			$O_1\text{-}O'_2(1)$	2.854	2.839	$O_1\text{-}O_3(1)$	2.367	2.374
			$O_3\text{-}O'_3(1)$	2.723	2.784			
Aver.	2.806	—	Aver.	2.708	2.681	Aver.	1.884	—

[a]Ref. [1].

Table S2. Structural parameters *a*, *b* and *c*, unit-cell volume, relative energies for the optimized YAB and low-lying Tm:YAB.

	Space group	*a* (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)	Δ*E* (eV)
YAB	*R*32	9.3542	9.3542	7.2673	550.697	
Tm:YAB	*P*321	9.3593	9.3593	7.2802	552.282	0
Isomer (a)	*P*321	9.3301	9.3301	7.2488	546.542	0.172
Isomer (b)	*P*321	9.4154	9.4154	7.3002	560.456	0.307
Isomer (c)	*C*2	16.3005	9.4486	7.4192	1142.65	0.378
Isomer (d)	*C*2	16.3307	9.4703	7.4483	1151.91	0.549

Table S3. The calculated energy levels (all in cm^{-1}) of free-ion Tm^{3+}.

$^{2s+1}L_J$	E_{obs}[a]	E_{calc}
$^3H_6$	0	0
$^3F_4$	5634	5634
$^3H_5$	8216	8216
$^3H_4$	12547	12548
$^3F_3$	14410	14410
$^3F_2$	15089	15089
$^1G_4$	21174	21174
$^1D_2$	28163	28163
$^1I_6$	35329	35329
$^3P_0$	—	35709
$^3P_1$	—	36801
$^3P_2$	38532	38532
$^1S_0$	—	75262

[a]Ref. [2].

Table S4. The calculated crystal field eigenvectors of the ground state $^3H_6$ for Tm^{3+} in YAB.

State No.	Statevector $\|^{2s+1}L_J\ M_J\rangle$
1	$0.88\|^3H_6\ 0\rangle + 0.32\|^3H_6\ -3\rangle - 0.32\|^3H_6\ 3\rangle$
2	$0.89\|^3H_6\ -1\rangle - 0.36\|^3H_6\ 2\rangle + 0.27\|^3H_6\ -4\rangle$
4	$-0.89\|^3H_6\ 2\rangle + 0.24\|^3H_6\ 5\rangle - 0.37\|^3H_6\ -1\rangle$
6	$0.56\|^3H_6\ -3\rangle - 0.56\|^3H_6\ 3\rangle - 0.42\|^3H_6\ 0\rangle + 0.30\|^3H_6\ -6\rangle + 0.30\|^3H_6\ 6\rangle$
7	$- 0.59\|^3H_6\ 3\rangle - 0.59\|^3H_6\ -3\rangle + 0.38\|^3H_6\ 6\rangle - 0.38\|^3H_6\ -6\rangle$
8	$0.64\|^3H_6\ -6\rangle + 0.64\|H_6\ 6\rangle + 0.27\|H_6\ 3\rangle - 0.27\|H_6\ -3\rangle + 0.19\|^3H_6\ 0\rangle$
9	$0.59\|^3H_6\ 6\rangle - 0.59\|^3H_6\ -6\rangle + 0.38\|^3H_6\ 3\rangle + 0.38\|^3H_6\ -3\rangle$
10	$- 0.96\|^3H_6\ -4\rangle + 0.25\|^3H_6\ -1\rangle - 0.12\|^3H_6\ 2\rangle$
12	$0.97\|^3H_6\ 5\rangle + 0.22\|^3H_6\ 2\rangle$

Table S5. The calculated spontaneous emission rates and MD oscillator strengths for transitions $\psi(SLJ\Gamma_i) \rightarrow \psi(S'L'J'\Gamma'_i)$ between different levels of Tm^{3+} in YAB.

$^{2S+1}L_J$ (Sta.) [a]	$S'L'J'$ (Sta.)	λ (nm)	A'_{MD} (s^{-1})	$P_{MD} \times 10^8$
$^3H_5$ (23)	$^3H_6$ (2)	1221	5.88	13.14
$^3H_5$ (24)		1217	10.90	24.18
$^3H_5$ (26)		1204	2.96	6.43
$^3H_5$ (24)	$^3H_6$ (4)	1228	8.19	18.52
$^3H_5$ (26)		1215	9.58	20.20
$^3H_5$ (26)	$^3H_6$ (6)	1227	11.23	25.38
$^3H_5$ (28)		1208	6.85	15.00
$^3H_5$ (26)	$^3H_6$ (7)	1232	11.00	25.04
$^3H_5$ (29)		1210	6.72	14.74
$^3H_5$ (30)		1205	2.30	5.00
$^3H_5$ (30)	$^3H_6$ (8)	1220	18.88	42.12
$^3H_5$ (29)	$^3H_6$ (9)	1226	2.90	6.52
$^3H_5$ (30)		1221	17.62	39.36
$^3H_5$ (28)	$^3H_6$ (10)	1234	6.96	15.88
$^3H_5$ (29)		1231	7.63	17.32
$^3H_5$ (32)		1217	6.92	15.35
$^3H_5$ (30)	$^3H_6$ (12)	1238	3.98	9.15
$^3H_5$ (32)		1229	18.93	42.87
$^3H_4$ (39)	$^3F_4$ (14)	1407	2.85	8.46
$^3F_3$ (43)		1136	4.42	8.56
$^3F_3$ (44)		1130	6.34	12.14
$^3F_3$ (48)		1124	2.38	4.52
$^3H_4$ (35)	$^3F_4$ (16)	1445	6.17	19.31
$^3F_3$ (44)		1131	3.84	7.37
$^3F_3$ (47)		1126	4.18	7.94
$^3F_3$ (48)		1125	4.11	7.79
$^3H_4$ (37)	$^3F_4$ (17)	1454	2.61	8.26
$^3F_3$ (43)		1155	3.01	6.02
$^3F_3$ (45)		1145	2.34	4.61
$^3F_3$ (47)		1143	4.00	7.81
$^3F_3$ (48)		1142	5.37	10.50
$^3H_4$ (39)	$^3F_4$ (19)	1445	2.82	8.81
$^3F_3$ (43)		1160	4.43	8.95
$^3F_3$ (45)		1151	10.91	21.67
$^3H_4$ (37)	$^3F_4$ (21)	1472	2.17	7.06
$^3F_3$ (44)		1157	7.15	14.34
$^3F_3$ (44)		1154	2.61	5.22
$^3F_3$ (45)		1153	5.00	9.89

$^3H_4$ (37)	$^3F_4$ (22)	1483	3.63	11.97
$^3F_3$ (42)		1447	2.35	7.38
$^3F_3$ (45)		1163	9.10	18.44
$^3F_3$ (47)		1161	3.40	6.86
$^3F_3$ (48)		1160	2.11	4.25
$^1G_4$ (55)	$^3H_5$ (23)	782	16.92	15.50
$^1G_4$ (56)		778	9.52	8.65
$^1G_4$ (58)		766	5.00	4.40
$^1I_6$ (75)		374	2.82	0.60
$^1I_6$ (76)		373	3.30	0.70
$^1G_4$ (55)	$^3H_5$ (24)	784	10.53	9.70
$^1G_4$ (56)		780	12.94	11.81
$^1G_4$ (58)		768	4.42	3.91
$^1G_4$ (61)		762	3.21	2.80
$^1I_6$ (76)		374	2.10	0.44
$^1G_4$ (56)	$^3H_5$ (26)	785	15.20	14.05
$^1G_4$ (58)		773	3.79	3.40
$^1G_4$ (61)		767	10.34	9.13
$^1G_4$ (61)	$^3H_5$ (28)	775	17.65	15.90
$^1G_4$ (63)		769	11.06	9.80
$^1I_6$ (69)		381	2.17	0.47
$^1I_6$ (70)		380	3.42	0.74
$^1G_4$ (58)	$^3H_5$ (29)	782	10.05	9.22
$^1G_4$ (60)		778	12.38	11.22
$^1G_4$ (61)		776	10.59	9.57
$^1I_6$ (74)		380	2.32	0.50
$^1G_4$ (56)	$^3H_5$ (30)	797	5.36	5.10
$^1G_4$ (58)		784	17.58	16.21
$^1G_4$ (61)		778	9.01	8.18
$^1I_6$ (81)		371	2.76	0.57
$^1G_4$ (58)	$^3H_5$ (32)	788	5.28	4.92
$^1G_4$ (60)		783	13.16	12.11
$^1G_4$ (63)		776	13.01	11.74
$^1I_6$ (78)		377	3.45	0.74
$^1G_4$ (56)	$^3H_4$ (34)	1178	7.52	15.65
$^1G_4$ (55)	$^3H_4$ (35)	1187	4.06	8.56
$^1G_4$ (61)		1139	3.40	6.60
$^1G_4$ (58)	$^3H_4$ (37)	1164	3.33	6.76
$^1G_4$ (63)		1137	2.44	4.73
$^1G_4$ (58)	$^3H_4$ (39)	1176	2.20	4.55
$^1G_4$ (61)		1162	3.30	4.13
$^1G_4$ (60)	$^3H_4$ (41)	1169	3.23	6.62
$^1G_4$ (61)		1166	6.09	12.41
$^1G_4$ (58)	$^3H_4$ (42)	1187	4.56	9.64

$^1G_4$ (63)		1160	4.51	9.10
$^1D_2$ (64)	$^3F_3$ (43)	749	20.37	17.11
$^3P_2$ (86)		424	19.68	5.32
$^3P_2$ (88)		421	3.78	1.01
$^1D_2$ (64)	$^3F_3$ (44)	751	16.57	14.02
$^1D_2$ (68)		743	3.40	2.81
$^3P_2$ (86)		425	9.86	2.68
$^3P_2$ (88)		422	8.60	2.30
$^3P_2$ (90)		419	2.53	0.67
$^1D_2$ (64)	$^3F_3$ (45)	752	8.62	7.32
$^1D_2$ (66)		745	11.31	9.42
$^3P_2$ (86)		426	8.25	2.24
$^3P_2$ (88)		423	16.66	4.46
$^1D_2$ (64)	$^3F_3$ (47)	754	3.43	2.92
$^1D_2$ (66)		746	8.80	7.35
$^1D_2$ (68)		745	8.84	7.36
$^3P_2$ (86)		426	10.62	2.90
$^3P_2$ (90)		420	12.04	3.18
$^1D_2$ (66)	$^3F_3$ (48)	747	10.45	8.74
$^1D_2$ (68)		746	10.27	8.57
$^3P_2$ (86)		426	5.43	1.48
$^3P_2$ (88)		423	9.14	2.45
$^3P_2$ (90)		420	7.65	2.02
$^1D_2$ (64)	$^3F_2$ (50)	782	11.16	10.23
$^1D_2$ (66)		774	5.89	5.29
$^1D_2$ (68)		773	2.93	2.62
$^3P_1$ (84)		463	4.46	1.43
$^1D_2$ (64)	$^3F_2$ (52)	788	5.63	5.23
$^1D_2$ (66)		780	5.29	4.82
$^1D_2$ (68)		779	6.23	5.67
$^3P_1$ (84)		465	3.02	1.00
$^1D_2$ (66)	$^3F_2$ (54)	785	13.88	12.81
$^3P_1$ (83)		470	2.97	0.98
$^3P_1$ (84)	$^1D_2$ (64)	1135	6.15	11.89
$^3P_2$ (86)		981	14.68	21.17
$^3P_2$ (88)		965	6.93	9.67
$^3P_1$ (83)	$^1D_2$ (66)	1174	3.26	6.74
$^3P_1$ (84)		1152	2.52	5.02
$^3P_2$ (86)		994	5.75	8.51
$^3P_2$ (88)		977	5.00	7.16
$^3P_2$ (90)		958	9.86	13.59
$^3P_1$ (83)	$^1D_2$ (68)	1176	4.00	8.28
$^3P_2$ (86)		995	5.43	8.06
$^3P_2$ (88)		978	20.33	29.16

[a]Only transitions between 300-10000 nm with emission rates $A'_{MD} > 2$ s^{-1} are listed.

Equation (S1): [3-4]

$$A_{ED(SLJ\to S'L'J')} = \frac{16\pi^3 e^2}{3\varepsilon_0 hc^3}\frac{\nu^3}{(2J+1)}\chi_{ED}\sum_{\lambda=2,4,6}\Omega_{(\lambda)}\left|\left\langle l^N SLJ\left\|U^{(\lambda)}\right\|l^N S'L'J'\right\rangle\right|^2 \quad \text{(S1)}$$

where ν is the transition frequency, n is the refractive index and χ_{ED} is the local-field correction for ED induced transitions with the form of $(n^2+1)^2/(9n)$ and $n(n^2+1)^2/9$ for absorption and emission transition, respectively. The Judd-Ofelt intensity parameters $\Omega_{(\lambda)}$ should be summed over λ=2,4,6 for a product with the even-rank reduced matrix elements of the $U^{(\lambda)}$ tensor operator.

Equation (S2): [3-4]

$$A_{MD} = \frac{\pi h e^2}{3\varepsilon_0 c^5 m_e^2}\frac{\nu^3}{g}\chi_{MD}\left|\left\langle l^N\psi\left\|L+g_e S\right\|l^N\psi'\right\rangle\right|^2 \quad \text{(S2)}$$

where g_e = 2.00232 is the gyromagnetic ratio of the electron and g is the degeneracy of the initial level. χ_{MD} is the local-field correction for MD induced transitions with the form of n and n^3 for the absorption and emission transition, respectively. ψ and ψ' are the statevectors for the initial and terminating levels for the $\psi \to \psi'$ transition, respectively. For transitions between J-multiplets, the statevector takes the form of $\psi(SLJ)$ with $g = (2J+1)$ while for transitions between crystal field levels, it takes the form of $\psi(SLJ\Gamma_i)$.

Equation (S3) for the radiative lifetime: [3-4]

$$\tau_{SLJ} = \frac{1}{\sum_{S'L'J'}(A_{ED(SLJ\to S'L'J')} + A_{MD(SLJ\to S'L'J')})} \quad \text{(S3)}$$

Equation (S4) for the branching ratio: [3-4]

$$\beta_{(SLJ\to S'L'J')} = \tau_{SLJ}\times[A_{ED(SLJ\to S'L'J')} + A_{MD(SLJ\to S'L'J')}] \quad \text{(S4)}$$

Equation (S5): [3-4]

$$P_{MD} = \frac{h\nu}{6m_e c^2}\frac{n}{(2J+1)}\left|\left\langle l^N SLJ\left\|L+g_e S\right\|l^N SLJ'\right\rangle\right|^2 \quad \text{(S5)}$$

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